

PATENT COOPERATION TREATY

PCT

NOTIFICATION OF ELECTION

(PCT Rule 61.2)

From the INTERNATIONAL BUREAU

To:

Commissioner
 US Department of Commerce
 United States Patent and Trademark
 Office, PCT
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 ETATS-UNIS D'AMERIQUE
 in its capacity as elected Office

Date of mailing (day/month/year) 15 May 2001 (15.05.01)	
International application No. PCT/AU00/01131	Applicant's or agent's file reference 40457935dvg
International filing date (day/month/year) 18 September 2000 (18.09.00)	Priority date (day/month/year) 17 September 1999 (17.09.99)
Applicant KOSIOR, Edward	

1. The designated Office is hereby notified of its election made:

☒ in the demand filed with the International Preliminary Examining Authority on:
 09 April 2001 (09.04.01)

☐ in a notice effecting later election filed with the International Bureau on:

2. The election ☒ was

☐ was not

made before the expiration of 19 months from the priority date or, where Rule 32 applies, within the time limit under Rule 32.2(b).

The International Bureau of WIPO 34, chemin des Colombettes 1211 Geneva 20, Switzerland Facsimile No.: (41-22) 740.14.35	Authorized officer G. Bähr Telephone No.: (41-22) 338.83.38
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INTERNATIONAL PRELIMINARY EXAMINATION REPORT

PCT

(PCT Article 36 and Rule 70)

Applicant's or agent's file reference 40457935	FOR FURTHER ACTION See Notification of Transmittal of International Preliminary Examination Report (Form PCT/IPEA/416).	
International Application No. PCT/AU00/01131	International Filing Date (day/month/year) 18 September 2000	Priority Date (day/month/year) 17 September 1999
International Patent Classification (IPC) or national classification and IPC Int. Cl. ⁷ B29B 17/00 // B29K 67:00		
Applicant VISY PLASTICS PTY LTD et al		

- This international preliminary examination report has been prepared by this International Preliminary Examining Authority and is transmitted to the applicant according to Article 36.
- This REPORT consists of a total of 3 sheets, including this cover sheet.
☒ This report is also accompanied by ANNEXES, i.e., sheets of the description, claims and/or drawings which have been amended and are the basis for this report and/or sheets containing rectifications made before this Authority (see Rule 70.16 and Section 607 of the Administrative Instructions under the PCT).

These annexes consist of a total of 14¹³ sheet(s).

- This report contains indications relating to the following items:

- | | | |
|------|-------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------|
| I | <input checked="" type="checkbox"/> | Basis of the report |
| II | <input type="checkbox"/> | Priority |
| III | <input type="checkbox"/> | Non-establishment of opinion with regard to novelty, inventive step and industrial applicability |
| IV | <input type="checkbox"/> | Lack of unity of invention |
| V | <input checked="" type="checkbox"/> | Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement |
| VI | <input type="checkbox"/> | Certain documents cited |
| VII | <input type="checkbox"/> | Certain defects in the international application |
| VIII | <input type="checkbox"/> | Certain observations on the international application |

Date of submission of the demand 9 April 2001	Date of completion of the report 16 November 2001
Name and mailing address of the IPEA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustalia.gov.au Facsimile No. (02) 6285 3929	Authorized Officer M. BREMERS Telephone No. (02) 6283 2052

I. Basis of the report

1. With regard to the **elements** of the international application:*
- ☐ the international application as originally filed.
- ☒ the description, pages , as originally filed,
pages , filed with the demand,
page 1 received on 12 November 2001 with the letter of 12 November 2001
pages 2-11 received on 25 October 2001 with the letter of 25 October 2001
- ☒ the claims, pages , as originally filed,
pages , as amended (together with any statement) under Article 19,
pages , filed with the demand,
pages 12-13 received on 25 October 2001 with the letter of 25 October 2001
- ☐ the drawings, pages , as originally filed,
pages , filed with the demand,
pages , received on with the letter of
- ☐ the sequence listing part of the description:
pages , as originally filed
pages , filed with the demand
pages , received on with the letter of
2. With regard to the **language**, all the elements marked above were available or furnished to this Authority in the language in which the international application was filed, unless otherwise indicated under this item.
These elements were available or furnished to this Authority in the following language which is:
- ☐ the language of a translation furnished for the purposes of international search (under Rule 23.1(b)).
- ☐ the language of publication of the international application (under Rule 48.3(b)).
- ☐ the language of the translation furnished for the purposes of international preliminary examination (under Rules 55.2 and/or 55.3).
3. With regard to any **nucleotide and/or amino acid sequence** disclosed in the international application, the international preliminary examination was carried out on the basis of the sequence listing:
- ☐ contained in the international application in written form.
- ☐ filed together with the international application in computer readable form.
- ☐ furnished subsequently to this Authority in written form.
- ☐ furnished subsequently to this Authority in computer readable form.
- ☐ The statement that the subsequently furnished written sequence listing does not go beyond the disclosure in the international application as filed has been furnished.
- ☐ The statement that the information recorded in computer readable form is identical to the written sequence listing has been furnished
4. ☐ The amendments have resulted in the cancellation of:
- ☐ the description, pages
- ☐ the claims, Nos.
- ☐ the drawings, sheets/fig.
5. ☐ This report has been established as if (some of) the amendments had not been made, since they have been considered to go beyond the disclosure as filed, as indicated in the Supplemental Box (Rule 70.2(c)).**

* Replacement sheets which have been furnished to the receiving Office in response to an invitation under Article 14 are referred to in this report as "originally filed" and are not annexed to this report since they do not contain amendments (Rules 70.16 and 70.17).

** Any replacement sheet containing such amendments must be referred to under item 1 and annexed to this report

V. Reasoned statement under Article 35(2) with regard to novelty, inventive step or industrial applicability; citations and explanations supporting such statement**1. Statement**

Novelty (N)	Claims 1-11	YES
	Claims	NO
Inventive step (IS)	Claims 1-11	YES
	Claims	NO
Industrial applicability (IA)	Claims 1-11	YES
	Claims	NO

2. Citations and explanations (Rule 70.7)

D1 US 5876644 A (NICHOLS et. al.) 2 March 1999
Column 3 line 43-column 4 line 28

The closest prior art document is D1. D1 discloses the features of claim 1 except for reducing the moisture content of the flakes to less than 0.1% w/w. Therefore, claim 1 is novel.

D1 allows for a decrease in intrinsic viscosity during extrusion because virgin PET is added to the melt to raise the intrinsic viscosity. At page 4 lines 13-26 of the present application it explains that it is important to remove the moisture from the flakes since excess water would lead to a reduction in the molecular weight and intrinsic viscosity of the resin. Therefore, in the present invention blending with virgin PET is not required. Consequently claim 1 is inventive.

Claims 2-11 are novel and inventive because they are appended back to claim 1.

PROCESS FOR PREPARING FOOD CONTACT GRADE POLYETHYLENE TEREPHTHALATE RESIN FROM WASTE PET CONTAINERS

Technical Field

5 This invention relates to methods for preparing polyethylene terephthalate (PET) resin from plastic waste that includes PET containers. It also relates to PET obtained according to the process.

Background to the Invention

10 PET is a widely used polymer or resin with a broad range of applications but which has a particularly widespread use as a beverage container or bottle. The use of PET for beverage containers has increased rapidly over the last decade and has to a large extent replaced conventional glass beverage containers especially for carbonated soft drinks. Part of the widespread acceptance of PET has been attributed to its ability to be used for food contact as well as its light weight relative to glass of comparable
15 strength and its ability to resist breakage.

 Over recent years environmental pressures have increased and there is a demand for the recycling of many materials, especially plastics. One common source of recyclable material is post consumer curbside waste. With PET containers most of the applications for recycled PET are for relatively low specification products that use
20 a mixture of thermoplastic resins or polymers including PET. In these applications removal of contaminants is not important. It is desirable that PET containers may be recycled to produce PET resin that is suitable for the same applications as virgin PET. For example, it is especially desirable that the recycled resin may be used for food contact applications. However, for such applications there are strict limits on the
25 presence of contaminants.

 Various methods have been proposed for recycling PET resin. One such method is disclosed in US Patent No. 5554657 which is assigned to the Shell Oil Company. In this patent a mixed polymer recycle stream that includes PET polymers is contacted with a solvent that selectively dissolves PET. This
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polymer solution is then separated from undissolved material and cooled to allow the precipitation of the PET resin. While this process leads to excellent quality product it is expensive as it involves the use of organic solvents which need to be recycled themselves. Other recycling methods involve the separation
5 of particulate contaminants by filtration of a molten polymer. This filtration method is facilitated by reducing the molecular weight and thus the intrinsic viscosity of the polymer to allow the molten material to flow more readily. However this reduction in molecular weight necessitates a final polymerisation or condensation reaction stage to produce PET of the required viscosity and
10 molecular weight. This method also requires the frequent replacement and/or cleaning of filters.

A further approach to recycling PET for food grade applications is disclosed in Australian Patent Application No. 9478299. In this invention beverage containers are produced having inner and outer skins. The inner skin
15 which is in contact with food is made from virgin PET and the outer skin is made from recycled PET resin. This invention removes the necessity for the recycled PET being suitable for food contact. However it is desirable that recycled PET can be used for direct food applications without using multiple skin production methods with their associated complexities and costs.

20 US Patent 5,876,644 discloses a process for preparing food contact grade PET. The process involves the surface cleaning of comminuted pieces of post consumer PET containers; followed by melting of the cleaned pieces; followed by extrusion to form a melt and then blending of this melt with a melt virgin polyester prepolymer. The combined melt is then solidified and polymerisation
25 is then effected while the pellets are in the solid state. The use of virgin PET prepolymer would have the effect of reducing the contaminant level as well as allowing solid state polymerisation to take place to achieve the desired intrinsic viscosity increase. It is an important feature of this earlier invention that molecular weight increase takes place in the solid state after extrusion. As this
30 process requires a post extrusion solid state increase in intrinsic viscosity a

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reduction in the intrinsic viscosity during extrusion is permitted or achieved by adding water prior to melting and extrusion (see column 7, lines 25-35).

PET originating from sorted collections of solid urban refuse can be contaminated with a range of materials. The PET will include both food contact grade PET such as containers as well as non food contact grade PET. The range of non PET materials include other polymers especially polyolefins such as HDPE. Other common contaminants are metals, particulate material such as dirt, glues, paper, inks and remnants of materials stored in the containers. It is desirable that food contact grade PET may be obtained from such collections of urban refuse.

Summary of the Invention

This invention provides in one form a process for preparing food contact grade PET from a waste stream containing PET and non PET materials comprising the following steps:

- 15 sorting at least some of the non PET materials from the waste stream;
- dividing the PET containers into flakes of preferable maximum size approximately 10mm;
- washing the flakes in a hot aqueous medium containing alkaline materials and surfactants, preferably non-ionic, to remove particulate and
- 20 absorbed contaminants from the surfaces of the flakes;
- de-watering and then drying the flakes to a moisture content of 0.1% w/w maximum, and more preferably 0.01% w/w maximum;
- optionally removing absorbed contaminants and moisture by heating and vigorously mixing the flakes under vacuum, preferably 1- 10 millibar, more
- 25 preferably 2 – 7 millibar and at a temperature less than the melting point of PET, preferably in the range 170-220°C for at least 30 minutes, preferably at least 60 minutes;
- melting the flakes in a screw extruder under vacuum to remove absorbed contaminant and;
- 30 extruding the molten material to form strands that are pelletised.

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Preferably the material in the extruder is maintained at 280 - 290°C with a residence time of less than 60 seconds.

Preferably the heating to remove the absorbed contaminants is attained by frictional forces from the vigorous mixing.

5 Detailed Description of the Invention

To meet FDA requirements for food contact grade PET the recycled PET must have contamination sufficiently low than such that the level of extractables is less than 10 ppb. As well as contaminants from the presence of non PET containers such as dirt, and other plastics, a range of materials may be adsorbed
10 into or absorbed onto PET surfaces. These contaminants can include organo metallic materials such as copper octoate. Absorbed materials may include polar and non polar organic materials that have a range of volatilities.

It is an important feature of the present invention that the majority of adsorbed and absorbed materials are removed while the PET material is in flake
15 form. We have found this facilitates the removal of contaminants that are generally either on or near the surface of the PET flakes. We have found that the removal of such contaminants after the material has become molten is much less effective as the contaminants tend to become buried in the resinous mass. It is also an important feature of the present invention that water content is
20 reduced to low levels and is further reduced during the vacuum venting of the PET melt in the screw extruder. We have found the low initial water level and the vacuum venting in the melt extruder enables the equilibrium water content to be reduced such that the molecular weight is increased. The presence of
25 linkage leading to reduced molecular weight and thus the intrinsic viscosity of the resin.

This invention will be further described by reference to preferred processes.

An urban solid waste stream consisting of baled bottles are passed
30 through a debaler that singulates the bottles so that they can be fed at a steady

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rate to the inlet of a pre-wash unit. The preferred pre-wash unit is one that utilises elevated temperatures and alkaline surfactants such as one like a Sorema Bottle Pre-wash unit. However similar units that have either a continuous or batch-wise mode of operation may also be used.

5 The feed rate is typically in the range 500 kgs to 2500 kgs per hour with 1500 kgs per hour being the optimum rate. The action of the pre-wash unit is to tumble the bottles using the rotary motion of the cylindrical tumbler unit about its longitudinal axis. Internal baffles in the tumbler ensure that all bottles are singulated by repeated impact of the bottles falling against the walls and baffles
10 while they are exposed to hot water and steam. The internal temperature is typically maintained in the range 90 to 100°C with temperatures greater than 95°C being preferred. The residence time in the pre-wash unit is generally in the range between 3 minutes and 15 minutes with a typical time being 5 minutes. The water in the pre-wash may include cleaning agents such as caustic
15 soda and non-foaming detergents. Typical concentrations of the caustic soda and detergent are 0.1 to 3% (ideally 0.5%) and 0.1 to 0.5% (ideally 0.2%) respectively.

The preferred detergent or surfactant is non-ionic.

The wash bottles are then de-watered by tumbling them in a cylindrical
20 tumbler or similar device that allows the freed dirt and other contaminants such as labels and closures to pass through the perforations in the walls of the tumbler. The water can be reused after it is filtered and treated to remove foreign materials. The residence time in this de-watering unit is in the range 3 minutes and 15 minutes with a typical time being 5 minutes.

25 At this stage the bottles are clean externally except for a film of water and are mostly free of plastic or paper labels through the action of the mechanical handling of the bottles, the hot water and the cleaning agents.

The PET bottles are then sorted. The preferred process uses automatic systems such as those made by Magnetic Separation Systems (MSS), ROFIN or
30 National Recovery Technologies Inc (NRT) although manual sorting can also be

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used. Particularly good results are achieved when a sequence of compositional analysis and sorting modules are used to sort the PET bottles to give a level of purity of no more than 20 ppm of PVC. The level of sorting of non PET should be to 99.998% purity. The MSS modules use modular sensors to detect the
5 presence of specific plastics and air jets to eject the bottles at a specific station.

The first module uses an X-ray absorption to detect the chlorine atom in PVC and the PVC bottles are ejected at this station. This module also removes aluminium cans due to their strong X-ray absorption.

The second module uses infra-red absorption to detect HDPE (high
10 density polyethylene) bottles and these are then ejected.

The third module uses near infra-red absorption to detect PET and in this module all the non PET bottles are ejected. This module will eject bottles such as PVC, HDPE, polypropylene, polystyrene and aluminium cans.

The fourth module uses X-ray absorption to detect the chlorine atom in
15 PVC and the PVC bottles are ejected at this station. This module also removes aluminium cans due to their strong X-ray absorption.

A manual inspection is used to finally check that only PET bottles proceed into the later stages of the process.

The sorted PET containers are then reduced in size using a wet grinder
20 such as a Sorema hot wash, separation and rinsing system or its equivalent.

The wet grinder uses multiple rotating knives to cut the PET bottles against stationary knives in the presence of water that is at ambient temperature or at elevated temperatures (from 10 to 40°C, with 15 to 20°C being most often used), and which will contain caustic soda and low foaming surfactants and
25 antifoam additives. Typical concentrations of the caustic soda and detergent is 0.1 to 3% (ideally 0.5%) and 0.1 to 0.5% (ideally 0.2%) respectively. Anti-foam use is related to surfactant level and is usually in the range 0.01 to 1%.

The PET bottles are cut against a screen with a hole size of 10mm to 30mm with 16 to 20 mm being the most common. This gives an intense
30 washing and simultaneous cutting effect on the PET bottles resulting in a range

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of average flake sizes that varies from 3mm to 12mm with the most numerous being under 8mm.

After grinding to this small size the mixture of PET flake and polypropylene particles (from closures and neck rings) is fed into a hot wash station such as Sorema Hot Wash Reactors (or similar) where the mix is
5 intensively washed for 10 to 20 minutes at temperatures from 75 to 95°C with 90°C being the ideal. The flakes are fed into the reactors at a liquid to plastic flake slurry ratio of 90/10 to 65/35 with 75/25 Volume/Volume being most common.

10 The reactors are designed to provide turbulent washing conditions where particles impinge on each other through the use of opposed-rotor, dual-rotor stirrers that are used in non-central positions to prevent laminar mixing from occurring, thus ensuring the most intense washing effect on the PET flakes.

After washing the flakes are separated from the wash solution by the use
15 of a centrifuge or screen, and the flakes are subjected to a sink-float separation in a tank of water where the polypropylene particles float due to their density being less than that of water (915 kg/m^3) and the PET particles sink due to their density being greater than that of water (1400 kg/m^3).

The separated PET flakes are then further rinsed at least twice in clean
20 water to remove the residual traces of surfactants and dilute contaminants. The pathway of the water and flakes is counter current to provide the maximum rising effect.

The PET flakes are then de-watered to give a very low level of moisture, i.e. down to 0.005% water.

25 This can be done by staged drying with fluidised bed driers to remove apparent moisture followed by conventional recirculating air driers, desiccant driers, agglomerators or other drying systems that may also use a dry gas to dry the PET at elevated temperatures (140 – 185°C).

The fluidised bed driers will remove the moisture from saturated levels
30 down to levels of less than 1% and typically 0.5%.

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The desiccant driers, agglomerators or other driers will reduce the moisture level to at least 0.01% i.e. 1000ppm of water with an ideal level of 0.005% of moisture, i.e. 500ppm. In conventional driers this may require the use of long residence times as well as high temperatures, eg. temperatures of the order of 120 to 175°C for 8 to 5 hours with 170°C for 5 hours proving optimum. The use of pre drying of the PET flakes is important as it leads to an increase rather than decrease in the intrinsic viscosity (IV) of the polymer in the following stages of the process. For example, the IV of the final PET pellet with the pre drying step was 0.833 versus 0.749 without compared to the IV of the flake itself of 0.767.

The dried flakes are then subjected to vacuum decontamination.

This process uses high levels of vacuum, preferably 1- 10 millibar, more preferably 2 – 7 millibar, while the PET is subjected to elevated temperatures (170 to 215°C) and mixing for controlled residence times of typically 1 hour, although longer times may also be useful. This decontamination can be performed in a shredder chamber modified to maintain a vacuum, or in a fluidising mixer modified to hold a vacuum. Frictional forces between flakes and parts of the equipment lead to heat build up and this is the preferred method of attaining the desired temperature. The impeller in the chamber is rotated at between 200 to 220 rpm converting mechanical energy into heat. Increasing the speed generates high temperatures with typically a temperature gradient, the higher temperatures being at the bottom. For example, when the impeller speed was 220 rpm the temperature at the bottom was 199°C, in the middle was 189°C and at the top 169°C.

Preferably the loading of the chamber with the PET flakes and the rotor speed are selected so that the chamber was filled to a sufficiently high level, approximately 70%, that flake introduced through a vacuum lock could reside at the top for a controlled residence time without the risk of immediately being mixed into the bulk of the flake and being extruded with only a short residence time. The conditions in the chamber were balanced so that the PET flake was

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progressively exposed to higher temperatures while under high vacuum and maintained at this condition for at least one hour after which it was introduced into the extruder.

5 The decontamination of the PET takes place in the mixer by the combined action of the vacuum, elevated temperature and the residence time of the PET under these conditions.

10 The decontaminated PET flakes are then fed to a single screw extruder with an extrusion screw designed for the processing of PET and capable of applying vacuum venting to the PET melt at 280 to 290°C. The process could be conducted in a similar twin screw extruder with vacuum venting or in a twin or multi-screw extruder with vacuum venting. The key requirement is the capability to melt the PET (melt temperature in the range 265 – 300°C, preferably 280°C) and to apply one or more stages of vacuum venting (at preferably 1 millibar or less) without applying excessive shear to the PET in the melt stage through excessive mechanical working of the melt. Excessive shear leads to a decrease in the IV. The application of the higher temperatures in the melt coupled with the vacuum venting allows removal of the least volatile fluids that may have been absorbed into the PET.

20 While this process has been described without the use of chemical chain extenders to increase the IV of the PET; these chemical materials may also be used. Chain extender materials are known and usually comprise one or more of a polycarboxylic acid or anhydride, a polyol and an esterification catalyst. For example, we have found a mixture of pyromellitic dianhydride, anhydride, pentaerythritol and antimony oxide in the weight ratios of 4:1:0.5 is a particularly useful chain extender composition. In the process described above the use of this chain extender composition has been able to increase the IV of the PET to 0.930 when used at 0.3% w/w of PET. Higher levels, eg 1.0% w/w increased the IV to 1.300.

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After melting and vacuum venting the melt is filtered by passing it through fine metal mesh filters (usually the mesh size is 120 mesh or finer) to remove any particles.

The extruded melt may then be converted to pellets typically 3mm using conventional techniques such as by using an underwater die face cutter or hot die face and water ring that quenches the melt into pellets as they are cut. Further steps may include crystallising the pellets and pre-drying the pellets prior to moulding. The crystallising is carried out by heating the PET pellets while they are kept moving via tumbling or agitation. The temperature is maintained at from 120°C to 170°C for between 10 minutes and 1 hour.

Pre drying is carried out by heating the pellets at elevated temperatures in hot gas that has a dew point of less than 40°C. The temperatures used typically vary from 140°C to 190°C for a duration that typically varies from 4 hours to 7 hours.

The effectiveness of the recycling process of the present invention is illustrated by introducing the following contaminants to PET containers:

toluene 10% v/v, chloroform 10% u/v, benzophenone 1% v/v, methyl stearate 1% v/v and copper octoate 1% v/v.

The concentrations of these contaminants after the various stages of the process steps of the present invention are set out in Table 1. These results show that after the process of the present invention contamination levels in the extruded pellets are acceptably low. The Table also shows the levels of extractables from PET bottles made from pellets prepared as described above.

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AMENDED SHEET
IPER/AU

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Table 1
Contaminant Levels (Ppm) In Washed Flake,
Extruded Pellets And Food Stimulant (10% Ethanol)

Contaminant	PET Flake Before Wash	PET Flake After Wash	Extruded PET Pellets	Levels in Food Stimulant (10% Ethanol) After the Migration test with Bottles made from PET Pellets
Toluene	1768.0	360.5	7.0	<0.01
Chloroform	612.5	52.3	24.8	<0.004
Benzophenone	713.3	175	54	<0.005
methyl stearate	81.2	16	1	<0.005
copper octoate	230.3	8	5.0	<0.001

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CLAIMS:

1. A process for preparing food contact grade PET from a waste stream containing PET and non PET materials comprising the following steps:
 - 5 sorting at least some of the non PET materials from the waste stream;
 - dividing the PET containers into flakes;
 - washing the flakes in a hot aqueous medium containing alkaline materials and surfactants to remove particulate and absorbed contaminants from the surfaces of the flakes;
 - 10 de-watering and then drying the flakes to a moisture content of 0.1% w/w maximum;
 - melting the flakes in a screw extruder under vacuum to remove absorbed contaminants; and
 - extruding the molten material to form strands that are pelletised.
- 15 2. A process according to claim 1 wherein there is a further heating and mixing step, before the extruder, that heats and vigorously mixes the flakes under vacuum at a temperature less than the melting point of PET.
3. A process according to claim 1 or claim 2 wherein the surfactants in the
20 flake washing step are non-ionic.
4. A process according to any one of claims 1 – 3 wherein the maximum moisture content of the flakes after the drying step is 0.01% w/w.
- 25 5. A process according to any one of claims 2 – 4 wherein the heating and mixing step is conducted at a reduced pressure of 1 – 10 millibar.
6. A process according to claim 5 wherein the pressure is in the range of
30 2 - 7 millibar.

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7. A process according to any one of claims 2 – 6 wherein the heating and mixing step is conducted at a temperature in the range 170 – 200°C for at least 30 minutes.
- 5 8. A process according to claim 7 wherein the heating and mixing step is conducted for at least 60 minutes.
9. A process according to any one of claims 1 – 8 wherein the material in the extruder is maintained at a temperature in the range 280 – 290°C for less
10 than sixty seconds at a reduced pressure of 1 millibar or less.
10. A process according to any one of claims 1 – 9 wherein a chemical chain extender is used to increase the molecular weight of the recycled PET.
- 15 11. Recycled food contact grade PET prepared according to a process as defined in any one of claims 1 – 10.

PROCESS FOR PREPARING FOOD CONTACT GRADE POLYETHYLENE TEREPHTHALATE RESIN FROM WASTE PET CONTAINERS

Technical Field

This invention relates to methods for preparing polyethylene terephthalate (PET) resin from plastic waste that includes PET containers. It also relates to PET obtained according to the process.

Background to the Invention

PET is a widely used polymer or resin with a broad range of applications but which has a particularly widespread use as a beverage container or bottle. The use of PET for beverage containers has increased rapidly over the last decade and has to a large extent replaced conventional glass beverage containers especially for carbonated soft drinks. Part of the widespread acceptance of PET has been attributed to its ability to be used for food contact as well as its light weight relative to glass of comparable strength and its ability to resist breakage.

Over recent years environmental pressures have increased and there is a demand for the recycling of many materials, especially plastics. One common source of recyclable material is post consumer curbside waste. With PET containers most of the applications for recycled PET are for relatively low specification products that use a mixture of thermoplastic resins or polymers including PET. In these applications removal of contaminants is not important. It is desirable that PET containers may be recycled to produce PET resin that is suitable for the same applications as virgin PET. For example, it is especially desirable that the recycled resin may be used for food contact applications. However, for such applications there are strict limits on the presence of contaminants.

Various methods have been proposed for recycling PET resin. One such method is disclosed in US Patent No. 5554657 which is assigned to the Shell Oil Company. In this patent a mixed polymer recycle stream that includes PET polymers is contacted with a solvent that selectively dissolves PET. This polymer solution is then separated from undissolved material and cooled to allow the precipitation of the PET resin. While this process leads to excellent quality product it is expensive as it involves the use of organic solvents which need to be recycled themselves. Other

recycling methods involve the separation of particulate contaminants by filtration of a molten polymer. This filtration method is facilitated by reducing the molecular weight and thus the intrinsic viscosity of the polymer to allow the molten material to flow more readily. However this reduction in molecular weight necessitates a final polymerisation or condensation reaction stage to produce PET of the required viscosity and molecular weight. This method also requires the frequent replacement and/or cleaning of filters.

A further approach to recycling PET for food grade applications is disclosed in Australian Patent Application No. 9478299. In this invention beverage containers are produced having inner and outer skins. The inner skin which is in contact with food is made from virgin PET and the outer skin is made from recycled PET resin. This invention removes the necessity for the recycled PET being suitable for food contact. However it is desirable that recycled PET can be used for direct food applications without using multiple skin production methods with their associated complexities and costs.

PET originating from sorted collections of solid urban refuse can be contaminated with a range of materials. These include other polymers especially polyolefins such as HDPE. Other common contaminants are metals, particulate material such as dirt, glues, paper, inks and remnants of materials stored in the containers. It is desirable that food contact grade PET may be obtained from such collections of urban refuse.

Summary of the Invention

This invention provides in one form a process for preparing food contact grade PET from a waste stream containing PET and non PET materials comprising the following steps:

- sorting at least some of the non PET materials from the waste stream;
- dividing the PET containers into flakes of preferable maximum size approximately 10mm;
- washing the flakes in a hot aqueous medium containing alkaline materials and surfactants, preferably non-ionic, to remove particulate and absorbed contaminants from the surfaces of the flakes;

de-watering and then drying the flakes to a moisture content of 0.1% w/w maximum, and more preferably 0.01% w/w maximum;

optionally removing absorbed contaminants and moisture by heating and vigorously mixing the flakes under vacuum, preferably 1- 10 millibar, more preferably 2 – 7 millibar and at a temperature less than the melting point of PET, preferably in the range 170-220°C for at least 30 minutes, preferably at least 60 minutes;

melting the flakes in a screw extruder under vacuum to remove absorbed contaminant and;

extruding the molten material to form strands that are pelletised.

Preferably the material in the extruder is maintained at 280 - 290°C with a residence time of less than 60 seconds.

Preferably the heating to remove the absorbed contaminants is attained by frictional forces from the vigorous mixing.

Detailed Description of the Invention

To meet FDA requirements for food contact grade PET the recycled PET must have contamination sufficiently low than such that the level of extractables is less than 10 ppb. As well as contaminants from the presence of non PET containers such as dirt, and other plastics, a range of materials may be adsorbed into or absorbed onto PET surfaces. These contaminants can include organo metallic materials such as copper octoate. Absorbed materials may include polar and non polar organic materials that have a range of volatilities.

It is an important feature of the present invention that the majority of adsorbed and absorbed materials are removed while the PET material is in flake form. We have found this facilitates the removal of contaminants that are generally either on or near the surface of the PET flakes. We have found that the removal of such contaminants after the material has become molten is much less effective as the contaminants tend to become buried in the resinous mass. It is also an important feature of the present invention that water content is reduced to low levels and is further reduced during the vacuum venting of the PET melt in the screw extruder. We have found the low initial water level and the vacuum venting in the melt extruder enables the equilibrium water content to be reduced such that the molecular weight is increased. The presence of excess levels of water at melt temperatures tends to cause hydrolysis of the ester

linkage leading to reduced molecular weight and thus the intrinsic viscosity of the resin.

This invention will be further described by reference to preferred processes.

An urban solid waste stream consisting of baled bottles are passed through a debaler that singulates the bottles so that they can be fed at a steady rate to the inlet of a pre-wash unit. The preferred pre-wash unit is a Sorema Bottle Pre-wash unit that utilises elevated temperatures and alkaline surfactants. However similar units that have either a continuous or batch-wise mode of operation may also be used.

The feed rate is typically in the range 500 kgs to 2500 kgs per hour with 1500 kgs per hour being the optimum rate. The action of the pre-wash unit is to tumble the bottles using the rotary motion of the cylindrical tumbler unit about its longitudinal axis. Internal baffles in the tumbler ensure that all bottles are singulated by repeated impact of the bottles falling against the walls and baffles while they are exposed to hot water and steam. The internal temperature is typically maintained in the range 90 to 100°C with temperatures greater than 95°C being preferred. The residence time in the pre-wash unit is generally in the range between 3 minutes and 15 minutes with a typical time being 5 minutes. The water in the pre-wash may include cleaning agents such as caustic soda and non-foaming detergents. Typical concentrations of the caustic soda and detergent are 0.1 to 3% (ideally 0.5%) and 0.1 to 0.5% (ideally 0.2%) respectively.

The preferred detergent or surfactant is non-ionic.

The wash bottles are then de-watered by tumbling them in a cylindrical tumbler or similar device that allows the freed dirt and other contaminants such as labels and closures to pass through the perforations in the walls of the tumbler. The water can be reused after it is filtered and treated to remove foreign materials. The residence time in this de-watering unit is in the range 3 minutes and 15 minutes with a typical time being 5 minutes.

At this stage the bottles are clean externally except for a film of water and are mostly free of plastic or paper labels through the action of the mechanical handling of the bottles, the hot water and the cleaning agents.

The PET bottles are then sorted. The preferred process uses automatic systems such as those made by MSS, ROFIN or NRT although manual sorting can also be

used. Particularly good results are achieved when a sequence of MSS Binary modules are used to sort the PET bottles to give a level of purity of no more than 20 ppm of PVC. The level of sorting of non PET should be to 99.998% purity. The MSS modules use modular sensors to detect the presence of specific plastics and air jets to eject the bottles at a specific station.

The first module uses an X-ray absorption to detect the chlorine atom in PVC and the PVC bottles are ejected at this station. This module also removes aluminium cans due to their strong X-ray absorption.

The second module uses infra-red absorption to detect HDPE (high density polyethylene) bottles and these are then ejected.

The third module uses near infra-red absorption to detect PET and in this module all the non PET bottles are ejected. This module will eject bottles such as PVC, HDPE, polypropylene, polystyrene and aluminium cans.

The fourth module uses X-ray absorption to detect the chlorine atom in PVC and the PVC bottles are ejected at this station. This module also removes aluminium cans due to their strong X-ray absorption.

A manual inspection is used to finally check that only PET bottles proceed into the later stages of the process.

The sorted PET containers are then reduced in size using a wet grinder such as a Sorema hot wash, separation and rinsing system or its equivalent.

The wet grinder uses multiple rotating knives to cut the PET bottles against stationary knives in the presence of water that is at ambient temperature or at elevated temperatures (from 10 to 40°C, with 15 to 20°C being most often used), and which will contain caustic soda and low foaming surfactants and antifoam additives. Typical concentrations of the caustic soda and detergent is 0.1 to 3% (ideally 0.5%) and 0.1 to 0.5% (ideally 0.2%) respectively. Anti-foam use is related to surfactant level and is usually in the range 0.01 to 1%.

The PET bottles are cut against a screen with a hole size of 10mm to 30mm with 16 to 20 mm being the most common. This gives an intense washing and simultaneous cutting effect on the PET bottles resulting in a range of average flake sizes that varies from 3mm to 12mm with the most numerous being under 8mm.

After grinding to this small size the mixture of PET flake and polypropylene particles (from closures and neck rings) is fed into Sorema Hot Wash Reactors (or similar) where the mix is intensively washed for 10 to 20 minutes at temperatures from 75 to 95°C with 90°C being the ideal. The flakes are fed into the reactors at a liquid to plastic flake slurry ratio of 90/10 to 65/35 with 75/25 Volume/Volume being most common.

The reactors are designed to provide turbulent washing conditions where particles impinge on each other through the use of opposed-rotor, dual-rotor stirrers that are used in non-central positions to prevent laminar mixing from occurring, thus ensuring the most intense washing effect on the PET flakes.

After washing the flakes are separated from the wash solution by the use of a centrifuge or screen, and the flakes are subjected to a sink-float separation in a tank of water where the polypropylene particles float due to their density being less than that of water (915 kg/m³) and the PET particles sink due to their density being greater than that of water (1400 kg/m³).

The separated PET flakes are then further rinsed at least twice in clean water to remove the residual traces of surfactants and dilute contaminants. The pathway of the water and flakes is counter current to provide the maximum rising effect.

The PET flakes are then de-watered to give a very low level of moisture, i.e. down to 0.005% water.

This can be done by staged drying with fluidised bed driers to remove apparent moisture followed by conventional recirculating air driers, desiccant driers, Erema agglomerators or other drying systems that may also use a dry gas to dry the PET at elevated temperatures (140 – 185°C).

The fluidised bed driers will remove the moisture from saturated levels down to levels of less than 1% and typically 0.5%.

The desiccant driers, Erema agglomerators or other driers will reduce the moisture level to at least 0.01% i.e. 1000ppm of water with an ideal level of 0.005% of moisture, i.e. 500ppm. In conventional driers this may require the use of long residence times as well as high temperatures, eg. temperatures of the order of 120 to 175°C for 8 to 5 hours with 170°C for 5 hours proving optimum. The use of pre drying of the PET flakes is important as it leads to an increase rather than decrease in

the intrinsic viscosity (IV) of the polymer in the following stages of the process. For example, the IV of the final PET pellet with the pre drying step was 0.833 versus 0.749 without compared to the IV of the flake itself of 0.767.

The dried flakes are then subjected to vacuum decontamination.

This process uses high levels of vacuum, preferably 1- 10 millibar, more preferably 2 – 7 millibar, while the PET is subjected to elevated temperatures (170 to 215°C) and mixing for controlled residence times of typically 1 hour, although longer times may also be useful. This decontamination can be performed in an Erema shredder chamber modified to maintain a vacuum, or in a fluidising mixer modified to hold a vacuum. Frictional forces between flakes and parts of the equipment lead to heat build up and this is the preferred method of attaining the desired temperature. The impeller in the chamber is rotated at between 200 to 220 rpm converting mechanical energy into heat. Increasing the speed generates high temperatures with typically a temperature gradient, the higher temperatures being at the bottom. For example, when the impeller speed was 220 rpm the temperature at the bottom was 199°C, in the middle was 189°C and at the top 169°C.

Preferably the loading of the chamber with the PET flakes and the rotor speed are selected so that the chamber was filled to a sufficiently high level, approximately 70%, that flake introduced through a vacuum lock could reside at the top for a controlled residence time without the risk of immediately being mixed into the bulk of the flake and being extruded with only a short residence time. The conditions in the chamber were balanced so that the PET flake was progressively exposed to higher temperatures while under high vacuum and maintained at this condition for at least one hour after which it was introduced into the extruder.

The decontamination of the PET takes place in the mixer by the combined action of the vacuum, elevated temperature and the residence time of the PET under these conditions.

The decontaminated PET flakes are then fed to a screw extruder, such as an Erema extruder, with an extrusion screw designed for the processing of PET and capable of applying vacuum venting to the PET melt at 280 to 290°C. The process could be conducted in a similar twin screw extruder with vacuum venting or in a twin or multi-screw extruder with vacuum venting. The key requirement is the capability to

melt the PET (melt temperature in the range 265 – 300°C, preferably 280°C) and to apply one or more stages of vacuum venting (at preferably 1 millibar or less) without applying excessive shear to the PET in the melt stage through excessive mechanical working of the melt. Excessive shear leads to a decrease in the IV. The application of the higher temperatures in the melt coupled with the vacuum venting allows removal of the least volatile fluids that may have been absorbed into the PET.

While this process has been described without the use of chemical chain extenders to increase the IV of the PET, these chemical materials may also be used. Chain extender materials are known and usually comprise one or more of a polycarboxylic acid or anhydride, a polyol and an esterification catalyst. For example, we have found a mixture of pyromellitic anhydride, pentaerythritol and antimony oxide in the weight ratios of 4:1:0.5 is a particularly useful chain extender composition. In the process described above the use of this chain extender composition has been able to increase the IV of the PET to 0.930 when used at 0.3% w/w of PET. Higher levels, eg 1.0% w/w increased the IV to 1.300.

After melting and vacuum venting the melt is filtered by passing it through fine metal mesh filters (usually the mesh size is 120 mesh or finer) to remove any particles.

The extruded melt may then be converted to pellets typically 3mm using conventional techniques such as by using an underwater die face cutter or hot die face and water ring that quenches the melt into pellets as they are cut. Further steps may include crystallising the pellets and pre-drying the pellets prior to moulding. The crystallising is carried out by heating the PET pellets while they are kept moving via tumbling or agitation. The temperature is maintained at from 120°C to 170°C for between 10 minutes and 1 hour.

Pre drying is carried out by heating the pellets at elevated temperatures in hot gas that has a dew point of less than 40°C. The temperatures used typically vary from 140°C to 190°C for a duration that typically varies from 4 hours to 7 hours.

The effectiveness of the recycling process of the present invention is illustrated by introducing the following contaminants to PET containers:

toluene 10% v/v, chloroform 10% u/v, benzophenone 1% v/v, methyl stearate 1% v/v and copper octoate 1% v/v.

The concentrations of these contaminants after the various stages of the process steps of the present invention are set out in Table 1. These results show that after the process of the present invention contamination levels in the extruded pellets are acceptably low. The Table also shows the levels of extractables from PET bottles made from pellets prepared as described above.

TABLE 1
CONTAMINANT LEVELS (PPM) IN WASHED FLAKE,
EXTRUDED PELLETS AND FOOD STIMULANT (10% ETHANOL)

Contaminant	PET Flake Before Wash	PET Flake After Wash	Extruded PET Pellets	Levels in Food Simulant (10% Ethanol) After the Migration test with Bottles made from PET Pellets
toluene	1768.0	360.5	7.0	<0.01
chloroform	612.5	52.3	24.8	<0.004
benzophenone	713.3	175	54	<0.005
methyl stearate	81.2	16	1	<0.005
copper octoate	230.3	8	5.0	<0.001


CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for preparing food contact grade PET from a waste stream containing PET and non PET materials comprising the following steps:
 - sorting at least some of the non PET materials from the waste stream;
 - dividing the PET containers into flakes;
 - washing the flakes in a hot aqueous medium containing alkaline materials and surfactants to remove particulate and absorbed contaminants from the surfaces of the flakes;
 - de-watering and then drying the flakes to a moisture content of 0.1% w/w maximum;
 - melting the flakes in a screw extruder under vacuum to remove absorbed contaminants; and
 - extruding the molten material to form strands that are pelletised.
2. A process according to claim 1 wherein there is a further heating and mixing step, before the extruder, that heats and vigorously mixes the flakes under vacuum at a temperature less than the melting point of PET.
3. A process according to claim 1 or claim 2 wherein the surfactants in the flake washing step are non-ionic.
4. A process according to any one of claims 1 – 3 wherein the maximum moisture content of the flakes after the drying step is 0.01% w/w.
5. A process according to any one of claims 2 – 4 wherein the heating and mixing step is conducted at a reduced pressure of 1 – 10 millibar.
6. A process according to claim 5 wherein the pressure is in the range of 2 - 7 millibar.

7. A process according to any one of claims 2 – 6 wherein the heating and mixing step is conducted at a temperature in the range 170 – 200°C for at least 30 minutes.
8. A process according to claim 7 wherein the heating and mixing step is conducted for at least 60 minutes.
9. A process according to any one of claims 1 – 8 wherein the material in the extruder is maintained at a temperature in the range 280 – 290°C for less than sixty seconds at a reduced pressure of 1 millibar or less.
10. A process according to any one of claims 1 – 9 wherein a chemical chain extender is used to increase the molecular weight of the recycled PET.
11. Recycled food contact graded PET prepared according to a process as defined in any one of claims 1 – 10.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/AU00/01131

A. CLASSIFICATION OF SUBJECT MATTER		
Int. Cl. ⁷ : B29B 17/00 // B29K 67:00		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED		
Minimum documentation searched (classification system followed by classification symbols) B29C 17/00, 17/02		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPAT: IPC as above and keywords: PET, dry, recycl, wash and similar terms		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,Y	US 5876644 A (NICHOLS et. al.) 2 March 1999 Column 3 line 43-column 4 line 28	1-11
X,Y	EP 698462 A (ISELL S.A.) 28 February 1986 See Derwent Abstract Accession Number 96-118071/13	1-11
Y	US 5503790 A (CLEMENTS) 2 April 1996 Column 4 lines 3-16 and 48-57	1-11
<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C <input checked="" type="checkbox"/> See patent family annex		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 10 October 2000		Date of mailing of the international search report 18 OCT 2000
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaaustralia.gov.au Facsimile No. (02) 6285 3929		Authorized officer  M. BREMERS Telephone No : (02) 6283 2052

INTERNATIONAL SEARCH REPORT

International application No.

PCT/AU00/01131

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4092458 A (HOFFMAN) 30 may 1978 Column 1 line27-37	1-11
A	FR 2599665 A (RHONE-POULENC FIBRE) 11 December 1987 See Derwent Abstract Accession Number 88-037851/06	
	US 587664 and EP 698462 can each be combined with US 5503790 and US 4092458.	

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/AU00/01131

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report			Patent Family Member			
US	5876644	NONE				
EP	698462	LU	88522	LU	88597	
US	5503790	US	5693278	US	5849381	
US	4092458	BE	841847	CA	1089616	DE 2621596
		FR	2310852	GB	1515438	IT 1063588
		JP	51139855	LU	74956	NL 7605164
FR	2599665	NONE				
						END OF ANNEX